

Micro Determination of a Low Degree of Stearoyl Substitution in Partially-Stearoylated Cotton Fabric

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ABSTRACT

A rapid, direct, sensitive method of analysis of cellulose esters of long-chain fatty acids has been developed. The method consists of saponification with propanolic potassium hydroxide, neutralization by passage through a microcolumn containing an acid-coated solid support, and glc analysis of the liberated fatty acids. The method affords determination of the stearic constituent as low as one mg stearoyl group per gram of cloth.

Introduction

Isopropenyl stearate is an effective acylating agent for the stearoylation of cotton fabric, as reported in an accompanying paper [6]. One of the major advantages of incorporating the long fatty-chain component of this enol ester in cotton is the development of excellent water repellency with no significant alteration of the fabric's mechanical properties. The amount of chemically-bound fatty acyl moiety responsible for this modification cannot be weighed directly—*i.e.*, the error involved in determining the moisture regain is of the same magnitude as the add-on.

In our initial determination of the degree of substitution (DS) we used the procedure reported by Berni *et al.* [1] to obtain a quantitative measurement of the stearoyl groups chemically bound to the cloth. Their method entails saponification of the partial esters of cellulose with tetramethylammonium hydroxide followed by gas liquid chromatographic (glc) analysis of the methyl esters that are generated in the injection port by pyrolysis of the quaternary ammonium salts. While satisfactory values were obtained in our preliminary use of the method, the long saponification times (16 h) were inconvenient, and the method was considered costly in time for multi-sample or routine analyses. Also the conversion of a carboxylic acid to an ester for glc analysis is often unnecessary, since direct analysis of monobasic aliphatic acids on polyester columns containing phosphoric acid is a common technique [2]. It was therefore desired to have available a simple alternative procedure for the rapid, direct microanalysis of the fatty acids liberated by saponification by use of a common base like potassium hydroxide in place of the strongly odoriferous tetramethylammonium hydroxide.

A simple microanalytical procedure has been in extended use at this laboratory for the direct glc determination of complex mixtures of long-chain fatty acids. The method is capable of high resolution and has given excellent separations and quantitation of many complex mixtures [3, 5]. In its adaptation to the analysis of stearic acid liberated from stearoylated cloth, the technique of neutralizing the soap and extracting the liberated fatty acids in one step was devised as described in the experimental section. This approach is considered superior to the more conventional liquid-liquid extraction routine for recovery of the fatty acids, owing to advantages derived by (a) shorter extraction times, (b) reduced losses in manipulative operation, and (c) utilization of inexpensive disposable glassware.

A rapid, quantitative saponification and isolation of the stearic acid became the major problem requiring resolution. This was accomplished in 2 h at 95°C with normal propanolic potassium or in 4.5 h at 65°C with normal methanolic potassium hydroxide (Table I).

TABLE I. Effect of time on alcoholic KOH saponification of stearoylated cloth.

Time, h	Stearic acid ^a	
	MeOH method ^b	PrOH method ^c
1	0.41	0.75
1.5	0.83	
2		1.08
2.5	0.95	
3		1.06
3.5	1.02	
4.5	1.09	
5.5	1.08	

^a mg found per g of cloth.

^b 1 *N* MeOH at 65°C.

^c 1 *N* PrOH at 95°C.

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The time of work-up and glc analysis described in the experimental section was about 30 min. Thus, the total analysis by the propanolic procedure was completed in about 2.5 h. Saponification values in the comparative alcoholic solvents were in excellent agreement, since the same limiting values were attained for the two runs. Average deviation for the limiting values was less than 2%. Resaponification of deacylated samples gave no further change, indicating complete removal of acyl groups [1].

This method of analysis was used to determine the DS of cloth acylated with isopropenyl stearate under various conditions [6]. The DS and the corresponding water repellencies are listed in Table II. The values reveal the low degree of add-on that is capable of imparting water repellency. The rapid and sensitive analytical procedure thus provides a reliable measurement of trace amounts of fatty acids when incorporated as modifying agents in fabric.

TABLE II. Degrees of substitution in stearoylated fabric.

Mode of fabric treatment ^a	mg Stearoyl ^b 1.0 g Cloth	DS ^c	WR ^d
PTSA ^e : neat, iron-cured	1.47	0.0009	100
neat, oven-cured	2.12	0.0013	70
NSA ^f : neat; iron-cured	1.74	0.0011	80-90
neat; oven-cured	2.45	0.0015	50-80
solution; oven-cured	1.23	0.0007	50-70

^a Details of experimental treatment described in ref. [6].

^b Average of 4-8 samples.

^c Average value of degree of substitution. $DS = \frac{\text{Moles}(\text{stearoyl})}{\text{Moles}(\text{AGU})}$

$= \frac{(\text{g/M.W.})_{\text{stearoyl}}}{(\text{g/M.W.})_{\text{AGU}}}$; AGU = anhydroglucose unit; M.W._{stearoyl} = 267; M.W._{AGU} = 162.

^d Water repellency, AATCC Test Method 22-1971.

^e *p*-toluenesulfonic acid.

^f 2-naphthalenesulfonic acid.

Experimental

MATERIALS. Acid-washed Celite 545 was prepared by stirring 100 g Celite 545 (Fisher Sci. Co.², King of Prussia, PA) in one liter of 2 *N* HCl and filtering the mixture through a coarse sintered glass funnel. The cake was washed with distilled water until neutral, then with 500 ml acetone, and dried 16 h at 100°C. Celite-H₃PO₄ powder was prepared by grinding 25 g of acid-washed Celite 545 with 10 ml of 85% H₃PO₄ and 1.5 ml water in a mortar until homogeneous.

n-Pentane was purified by being scrubbed over a conc. H₂SO₄-Celite column and distilled [4]. Normal potassium hydroxide in *n*-propanol must be freshly prepared prior to use, owing to formation of an amber color in the solution on standing.

² Reference to brand or firm name does not constitute endorsement by the U. S. Department of Agriculture over others of a similar nature not mentioned.

DEGREE OF SAPONIFICATION OF STEAROYLATED CLOTH. Prior to acylation by isopropenyl stearate, the untreated print cloth was free of fatty acids and esters, as determined by the present analytical technique. A stearoylated fabric strip (1 × 6 in. (400-600 mg)) was placed in a 10-ml test tube and covered with 4 ml normal propanolic KOH or normal methanolic KOH. The tube was sealed with a Teflon septum and screw cap that permitted procurement of aliquots by syringe puncture. The sealed tube was placed in a constant-temperature oven at the boiling point of the alcohol solution. Aliquots were removed at intervals and analyzed for unesterified stearic acid as described below.

ISOLATION OF STEARIC ACID FROM SAPONIFICATION MEDIUM. A disposable column (so-called "super" pipette, 0.9 cm i.d. × 15 cm, Matheson Co.) was plugged with a small wad of purified glass wool [4] and pushed into the Celite powder until the tube was approximately half-filled. (If the glass wool is not purified, some free fatty acid will be obtained from it and afford higher values.) The powder was tamped tightly into a compact bed about 3 cm in length. This represents about 1.0-1.3 g of powder and contains approximately 4 millimoles of phosphoric acid. A 100-ml aliquot of saponification liquid was transferred by syringe onto the column by placing the needle tip lightly on the surface of the bed and slowly expelling the solution. (Some unwetted portion of the bed should remain after application of the solution. A bed 3-cm long will be more than adequate.) The column was then washed with *n*-pentane, the effluent was collected in a 2-ml screw-cap vial to its neck, and the solvent was removed under a stream of nitrogen. The residue was taken up in 100 μl of CS₂, and an aliquot was analyzed by glc.

QUANTITATIVE GAS-LIQUID CHROMATOGRAPHY. A linear standard stearic acid curve (integrator count *vs.* μg stearic acid) was prepared prior to analysis of the samples, and several points on the curve were rechecked following sample analysis. A 20 × .32-cm silanized stainless steel column packed with 7.5% stabilized ethylene glycol adipate containing 2% phosphoric acid on 90-100 mesh Anakrom ABS was used at 220°C. Helium flow rate was 30 ml/min at the column exit. Injection port and detector temperatures were 250°C. The area under the stearic acid peak was measured by a digital integrator.

RECOVERY STUDIES FROM THE MODEL SYSTEM. The efficiency of the method was checked by running recovery studies of pure stearic acid (NU-CHEK PREP, Inc., Elysian, Minn.). One ml of solution containing 0.308 μg of stearic acid per μl of carbon disulfide was taken to dryness under a nitrogen stream, and the residue was dissolved in 1 ml of the normal alcoholic

potassium hydroxide. Aliquots were removed and the potassium stearate was then neutralized on the Celite- H_3PO_4 column, and recoveries of the liberated stearic acid was determined directly by glc. From 15- and 30- μg samples of potassium soaps, recovery of stearic acid was essentially quantitative—i.e., 97 and 101%, respectively.

Literature Cited

1. Berni, R. J., Soignet, D. M., and Ward, T. L., Gas-Liquid Chromatographic Analyses of Cotton Partial Esters, *Textile Res. J.* **39**, 887-889 (1969).
2. Metcalfe, L. D., The Gas Chromatography of Fatty Acids and Related Long-Chain Compounds on Phosphoric Acid-Treated Columns, *J. Gas Chromatog.* **1**, (No. 1), 7-11 (1963).
3. Schwartz, D. P., Applications of Chromic Acid-Celite Columns to Lipid Analysis. Location of Double Bond Position in Submicro- and Microgram Amounts of Methyl Octadecenoates, *Anal. Biochem.* **74**, 320-328 (1976).
4. Schwartz, D. P., Glass Wool as a Potential Source of Artifacts in Chromatography, *J. Chromatography* **152**, 514-516 (1978).
5. Schwartz, D. P., New Micromethods for Isolating and Characterizing Lipid Constituents, *Agric. Sci. Rev.* **8**, 41-50 (1970).
6. Silbert, L. S., Serota, S., Maerker, G., Palm, W. E., and Phillips, J. G., Novel Acylation of Cotton Fabric with Isopropenyl Stearate and Effects on Water Repellency and Dimensional Stability, *Textile Res. J.* **48**, 422-426 (1978).